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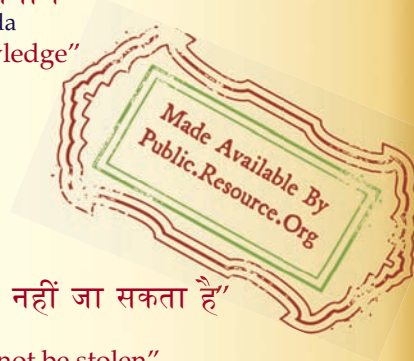
IS 1448-86 (1977): Methods of test for petroleum and its products, Part 86: Determination of total base number by potentiometric perchloric acid titration method [PCD 1: Methods of Measurement and Test for Petroleum, Petroleum Products and Lubricants]



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Bhartrhari—Nitiśatakam

“Knowledge is such a treasure which cannot be stolen”

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METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS [P: 86]

DETERMINATION OF TOTAL BASE NUMBER BY POTENTIOMETRIC PERCHLORIC ACID TITRATION METHOD

(First Reprint APRIL 1988)

UDC 665.6/7:543.257.1

Adapted, with permission, from the joint publication ASTM D 2896-73/IP 276/75

1. SCOPE

1.1 This method covers the determination of basic constituents in petroleum products by potentiometric titration with perchloric acid in glacial acetic acid.

1.2 For many materials the results obtained by this method will be similar to those obtained by IS: 1448 [P: 1]-1971*. With certain compounds such as strongly overbased oil additives and nitrogenous polymeric compounds, higher results may be obtained.

1.3 The constituents that may be considered to have basic characteristics include organic and inorganic bases; amino compounds; salts of weak acids, for example, soaps; basic salts of polyacidic bases; and salts of heavy metals.

2. SUMMARY OF METHOD

2.1 The sample is dissolved in an essentially anhydrous mixture of chlorobenzene and glacial acetic acid and titrated with a solution of perchloric acid in glacial acetic acid with a potentiometric titrimeter. A glass indicating electrode and a calomel reference electrode are used, the

*Methods of test for petroleum and its products: [P: 1] Neutralization number by potentiometric titration (*first revision*).

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latter being connected with the sample solution by means of a salt bridge. The meter readings are plotted against the respective volumes of titrating solution, and the end point is taken at the inflection in the resulting curve.

2.2 Occasionally, certain used oils give no inflection in the standard titration, in which case a back titration modification with sodium acetate titrant is employed.

3. DEFINITION

3.1 Total Base Number — The quantity of perchloric acid expressed in terms of the equivalent number of milligrams of potassium hydroxide that is required to neutralize all basic constituents present in 1 g of sample.

4. APPARATUS

4.1 Potentiometric Titrimeter — either automatic recording or manual.

4.2 Glass Electrode — pH 0 to 11, general purpose type.

4.3 Reference Electrode — sleeve-type saturated calomel electrode with nonaqueous salt bridge as described in 7 (*see* Note).

NOTE — Some reference electrodes with fritted or fibre diaphragms and some combined glass plus reference electrode systems are commercially available, such as the single-rod glass plus silver/silver chloride electrode assembly. During the development of this method, the use of electrodes of these types gave problems in some laboratories, but not in others. Accordingly, these electrodes are permitted in this method provided that the sodium perchlorate bridge is used; however, if stability or other problems arise with their use, the sleeve-type electrode should be used.

4.4 Stirrer — either mechanical or electrical, with variable speeds and with propeller or paddle of chemically inert material. If an electrical stirrer is used, it shall be grounded so that disconnecting or connecting the power to the motor will not produce a permanent change in meter reading during the course of titration. A magnetic stirrer with stirring bar may be used provided it meets the above conditions.

4.5 Burette — 10- or 20-ml capacity, graduated in 0.05 ml divisions and calibrated with an accuracy of ± 0.02 ml, or an automatic burette of similar accuracy.

4.6 Titration Beaker — of 250- or 300-ml capacity, made of borosilicate glass. The tall form beaker is particularly suitable.

4.7 Titration Stand — a suitable stand to support the beaker, electrodes, stirrer, and burette. An arrangement that allows for the removal of the beaker without disturbing the electrodes, burette and stirrer is desirable (*see* Note).

NOTE — Some apparatus may be sensitive to interference by static electricity, shown by erratic movements of recorder pen or meter indicator, when the titration assembly (beaker and electrodes) is approached by the operator. In this case surround the beaker closely with a cylinder of copper gauze which is electrically grounded (earthed).

5. QUALITY OF REAGENTS

5.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS: 1070-1977*) shall be used in tests.

NOTE — ' Pure chemicals ' shall mean chemicals that do not contain impurities which affect the results of analysis.

5.2 Acetic Acid — glacial (*see* Note).

NOTE — *Caution:* Acetic acid, acetic anhydride, and chlorobenzene are toxic and irritant. Carry out all operations involving the use of these material in a well-ventilated area, preferably under a hood.

5.3 Acetic Anhydride — *See* Note under 5.2.

5.4 Chlorobenzene — *See* Note under 5.2.

5.5 Perchloric Acid — standard acetous solution (0.1 N). Mix 8.5 ml of 70 to 72 percent perchloric acid (or 10.2 ml of 60 to 62 percent perchloric acid) with 500 ml of glacial acetic acid and 30 ml (or 38 ml if the 60 to 62 percent perchloric acid is used) of acetic anhydride (*see* Note 1). Dilute to 1 litre with glacial acetic acid (*see* Note 2). Allow the solution to stand for 24 hours before standardization.

NOTE 1 — Excess acetic anhydride shall be avoided to prevent acetylation of any primary or secondary amines which may be present.

NOTE 2 — *Caution:* This perchloric acid solution is not hazardous under the conditions of this test. However, concentrated perchloric acid is a powerful oxidizing agent when heated and forms explosive mixtures when heated with organic matter. Great care should be taken to avoid contact with organic matter under conditions that may result in subsequent drying or heating, and spills should be washed immediately and thoroughly with water.

5.5.1 Standardization of Perchloric Acid — Heat a quantity of potassium hydrogen phthalate in an oven at 120°C for 2 hours and allow it to cool. Take 0.1 to 0.2 g of the potassium hydrogen phthalate weighed to the nearest 0.1 mg and dissolve it in 40 ml of warm glacial acetic acid. Add 80 ml of chlorobenzene, cool, and titrate with 0.1 N perchloric acid, using the electrode system and procedures given in 7.1 to 7.4 and 8.4 to 8.7. Detect the end point by the same procedure as will be used for base number determination (*see* 9.2). Carry out a blank titration on 40 ml of glacial acetic acid plus 80 ml of chlorobenzene (*see* 8.8). Calculate the normality (*N*) of the perchloric acid as follows:

$$N = \frac{1\,000\,M}{204.23 (V_1 - V_0)}$$

*Specification for water for general laboratory use (*second revision*).

where

M = mass in g of potassium hydrogen phthalate,

V_1 = volume in ml of perchloric acid used, and

V_0 = volume in ml of perchloric acid corresponding to V_1 for the blank titration.

NOTE — Because of the relatively large coefficient of cubic expansion of organic liquids, the acetous perchloric acid solution should be used within $\pm 5^\circ\text{C}$ of the temperature at which it was standardized. If used at a temperature more than 5 degrees higher, multiply the volume used by the factor $1 - 0.001 t$. If used at a temperature more than 5 degrees lower, multiply by the factor $1 + 0.001 t$ (where t is the difference in degrees Celsius between temperatures of standardization and use, and is always positive).

5.6 Potassium Hydrogen Phthalate

5.7 Sodium Perchlorate Electrolyte — Prepare a saturated solution of sodium perchlorate (see Note) in glacial acetic acid. An excess of undissolved sodium perchlorate should always be present at the bottom of the solution.

NOTE — *Caution:* Sodium perchlorate is toxic and irritant. It is also a powerful oxidizing agent when heated. Great care should be taken to avoid contact with organic matter under conditions that may result in subsequent drying or heating, and spills should be washed immediately and thoroughly with water.

5.8 Titration Solvent — Add 1 volume of glacial acetic acid to 2 volumes of chlorobenzene (see Note under 5.2).

5.9 Sodium Carbonate — anhydrous.

5.10 Sodium Acetate Solution — 0.1 N acetous (for back titration see 11). Dissolve 5.3 g of anhydrous sodium carbonate in 300 ml of acetic acid. Dilute to 1 litre with acetic acid after solution is complete.

5.10.1 Standardization of Sodium Acetate Solution — Use the required volumes of titration solvent and 8.00 ml of 0.1 N acetous perchloric acid. Titrate with 0.1 N sodium acetate, using the electrode system and procedure given in 7.1 to 7.4 and 8.4 to 8.7. Detect the end point by the same procedure as will be used for base number determination (see 9.2). Calculate the normality (N_1) of the sodium acetate solution by the following formula:

$$N_1 = \frac{(8.00 - V_0) N}{V_2}$$

where

V_0 and N are as defined in 5.5.1, and

V_2 = volume in ml of standard acetous sodium acetate used in the standardization.

6. PREPARATION OF SAMPLE

6.1 It is essential to ensure that the sample is representative since any sediment may be acidic or basic or have adsorbed acidic or basic material from the liquid phase. If necessary, samples may be warmed to aid mixing. Used oils should be vigorously shaken to ensure homogeneity before preparing the test sample.

7. PREPARATION OF ELECTRODE SYSTEM

7.1 Preparation of Electrodes — If the calomel electrode is to be changed from aqueous bridge to nonaqueous, drain out the aqueous solution, wash out all crystals of potassium chloride with water, then rinse the outer jacket (salt bridge) several times with sodium perchlorate electrolyte. Finally fill the outer jacket with sodium perchlorate electrolyte up to the filling hole. When using the sleeve-type electrode, carefully remove the groundglass sleeve and thoroughly wipe both ground surfaces. Replace the sleeve loosely and allow a few drops of electrolyte to drain through to flush the groundglass joint and to wet the ground surfaces thoroughly with electrolyte. Set the sleeve firmly in place, refill the outer jacket with the sodium perchlorate electrolyte, and rinse the electrode with chlorobenzene. When in use, the electrolyte level in the calomel electrode should be kept above that of the liquid in the titration beaker to prevent entry of contaminants into the salt bridge. When not in use, fill the calomel electrode with sodium perchlorate electrolyte solution, leave the bung in the filling orifice, and immerse both electrodes in distilled water, keeping the level of the electrolyte above that of the distilled water.

7.2 Testing of Electrodes — Test the titrimeter-electrode combination when first put into use or when new electrodes are installed and retest at intervals thereafter as follows:

Dip the electrodes into a well-stirred mixture of 100 ml of glacial acetic acid plus 0.2 g of potassium hydrogen phthalate and record the titrimeter reading. Rinse the electrode with chlorobenzene and immerse in 100 ml of glacial acetic acid plus 1.5 ml of 0.1 N perchloric acid. The difference between readings should be at least 0.30 V.

7.3 Cleaning of Electrodes — Following a titration, first wash the electrodes with chlorobenzene-acetic acid solvent to remove any adhering oily material from the previous titration, then with water, to dissolve any sodium perchlorate that may have formed around the sleeve of the calomel electrode and to restore the aqueous gel layer of the glass electrode. Rinse again with titration solvent. Before starting a series of sample titrations, follow this rinsing procedure, then run one or two blank titrations on the solvent to condition the electrodes. Repeat the blank titrations, if necessary.

7.4 Maintenance of Electrodes — If there is reason to believe that the glass electrode has become contaminated, it may be cleaned by immersing in cold chromic acid cleaning solution for five minutes, followed by thorough water washing. After this cleaning treatment, test the electrode as described in 7.2. The calomel electrode can be cleaned by draining and refilling with fresh sodium perchlorate solution. Maintain the electrolyte level in the calomel electrode above that of the liquid in the titration beaker at all times. Do not allow the electrodes to remain immersed in titration solvent for any appreciable period of time between titrations. While the electrodes are not extremely fragile, handle them carefully at all times and particularly avoid scratching the glass electrode.

8. PROCEDURE

8.1 Calculate the quantity of sample required from its expected Total Base Number (TBN) from the following formula:

$$\text{Approximate mass of sample in g} = 28 / \text{expected TBN}$$

NOTE — For a possible exception, see Note under 11.2.

8.1.1 Weigh the sample into the titration beaker, applying the limits shown as follows. A maximum of 20 g should be taken for analysis:

<i>Mass of Sample</i>	<i>Precision of Weighing</i>
g	g
10 to 20	0.05
5 to 10	0.02
1 to 5	0.005
0.25 to 1.0	0.001
0.1 to 0.25	0.0005

8.2 Add 120 ml of titration solvent.

8.3 Place the beaker on the titration stand and stir the solution until the sample has dissolved (see Note).

NOTE — If solution of the sample proves difficult, dissolve in 80 ml of chlorobenzene in the titration beaker, then add 40 ml of glacial acetic acid. Many used oils contain some solid material which will not dissolve. The presence of this undissolved material will not affect the test result.

8.4 Prepare the electrodes as described in 7.1, 7.2 and 7.3. Position the electrodes in the solution so that they are immersed as far as possible. Continue the stirring throughout the determination at a rate sufficient to produce vigorous agitation without spattering and without stirring air into the solution. Adjust the titrimeter so that it reads in the upper part of the millivolt scale; for example, 700 mV. For simple titrimeters without

this adjustment, it may be necessary to incorporate a source of potential in series with the electrode. A 1.5-V dry cell and potential divider is suitable.

8.5 Fill the burette with 0.1 N perchloric acid solution and place the burette in position in the titration assembly, taking care that the tip is immersed below the level of the surface of the liquid in the beaker. Record the initial burette and titrimeter (cell potential) readings.

8.6 Titrations

8.6.1 Manual Titration — Add suitable small portions of titrant and after waiting until a constant potential has been established (*see* Note), record the burette and titrimeter readings. At the start of the titration and in any subsequent regions (inflections) where 0.1 ml of titrant consistently produces a total change of more than 0.03 V (corresponding to 0.5 pH scale unit) in the cell potential, add 0.05-ml portions. In the intermediate regions (plateaux) where 0.1-ml increments change the potential by less than 0.03 V, add large portions sufficient to produce a total potential change approximately equal to, but not greater than 0.03 V. Titrate in this manner until the potential changes less than 0.005 V (corresponding to 0.1 pH scale unit) per 0.1 ml.

NOTE — Consider the cell potential constant when it changes less than 0.005 V/minutes.

8.6.2 Automatic Recording Titration — Adjust the instrument in accordance with the manufacturer's instructions and set the titration speed at 1.0 ml/minute, *Max*.

8.7 On completion of the titration, remove the beaker and rinse the electrodes and burette tip with chlorobenzene-acetic acid titration solvent, then with water, then again with solvent (*see* 7.3). Store in water when not in use (*see* 7.1).

8.8 For each set of samples make a blank titration on 120 ml of titration solvent. For a manual titration add 0.1 N perchloric acid in 0.05-ml increments, waiting between each addition until a constant cell potential is established. Record titrimeter and burette readings after each increment. Follow the procedure in 8.6.2 for an automatic titration.

9. CALCULATION

9.1 For a manual titration, plot the volumes of the acid added against the corresponding titrimeter readings.

9.2 Interpret the end point from the graph obtained from the manual or automatic titration. The end point is the midpoint of the inflection, that point at which the curve changes from concave to convex. A useful but not mandatory guide is that the end point should be preceded and followed by a deflection of at least 50 mV/ml of titrant.

9.3 When there is no inflection point or only a very poor one, proceed to 'back titration' method prescribed in 11. The inflection obtained during back titration preferably should meet the criteria described in 9.2.

9.4 Calculate the total base number (TBN) as follows:

$$\text{Total base number (TBN), mg KOH/g} = \frac{(V_4 - V_3) \times N \times 56.1}{M}$$

where

V_4 = volume in ml of perchloric acid used to titrate the sample to the inflection point on the titration curve,

V_3 = volume in ml of perchloric acid used corresponding to V_4 for blank titration at same potential as sample,

N = normality of perchloric acid solution, and

M = mass in g of the sample.

10. REPORT

10.1 Report the result as the total base number (TBN) by IS : 1448 [P : 86]-1977.

11. BACK TITRATION

11.1 Some used oils give no inflection point or only a very poor one with the method as described above. When this situation is encountered, the following modified method may be used. In this modified method, excess standard perchloric acid solution is added to the sample, then the excess perchloric acid is back titrated with standard sodium acetate solution.

11.2 Weigh accurately the amount of sample specified in 8.1 and 8.1.1 (see Note) into the titration beaker.

NOTE — The sample size for the back titration modification should not exceed 5 g. If, with a 5-g sample, no inflection point is found, reduce the sample size to 3 g and repeat the analysis. Reducing the sample size generally improves the clarity of the inflection point. However, it shall be noted that the cooperative work which led to the precision statement (see 12.1.1 and 12.1.2) employed a sample size of 5 g maximum.

11.3 Dissolve the sample in 80 ml of chlorobenzene (see Note under 8.3) and add 40 ml of acetic acid.

11.4 Use a volumetric burette or pipette to add accurately 8.00 ml of standard 0.1 N acetous perchloric acid solution to the beaker. [The standard perchloric acid solution shall be in excess. If necessary, add more than 8.00 ml and correct accordingly (see 11.7)].

11.5 Stir the contents of the beaker for 2 minutes.

11.6 Titrate the unneutralized perchloric acid with standard 0.1 N acetous sodium acetate solution. Carry out the titration in the same manner as described in 8. For the back titration, the starting point will be in the range of 0-100 mV.

11.7 Instead of weighing out a separate sample and proceeding through 11.6, the back titration procedure can be used on a sample being titrated as in 8.1 to 8.6.2, provided that the sample size did not exceed .5 g (see Note under 11.2). When it is apparent from the forward titration that a satisfactory inflection is not present, note the volume of standard perchloric acid used, then proceed with 11.6. The standardization (see 5.10.1) should be modified to coincide with the volume of standard perchloric acid used.

11.8 Calculate the total base number (TBN) from the following formula:

$$\text{Total base number (TBN), mg KOH/g} = \frac{(V_2 - V_s) N_1 \times 56.1}{M}$$

where

V_2 and N_1 are as defined in 5.10.1,

V_s = volume in ml of standard acetous sodium acetate used in the sample titration,

M = mass in g of the sample.

11.9 Report the results as Total Base Number (TBN) by Back Titration Modification of IS : 1448 [P : 86]-1977.

12. PRECISION

12.1 The following criteria should be used for judging the acceptability of results (95 percent confidence).

12.1.1 Repeatability — Duplicate results by the same operator should be considered suspect if they differ by more than the following percentage of mean total base number:

	Percent
Fresh oils and additive concentrates:	
Total base number to 59.9	5
Total base number greater than 59.9	3
Used oils on which are employed the forward titration	5
Used oils which require the back titration	24

12.1.2 Reproducibility — Results submitted by two laboratories should not be considered suspect unless they differ by more than the following percentages of mean total base number:

	<i>Percent</i>
Fresh oils and additive concentrates:	
Total base number to 59.9	6
Total base number greater than 59.9	4
Used oils on which are employed the forward titration	15
Used oils which require the back titration	32

NOTE — The ranges of total base number values for which the above precision values were established are given in Appendix A.

APPENDIX A

(Clause 12.1.2)

TEST COVERAGE

A-1. During the development of this method, co-operative testing was done on samples covering a wide range of types of oils, of additive concentrates which are used to prepare these oils, and of services for the oils. Even so, however, it was not possible to cover the complete range of total base numbers. It is believed that reasonable interpolation and extrapolation from the ranges used will not introduce serious errors in the precision.

The ranges used were:

Fresh oils	Total base number of 5.5-13.5
Additive concentrates	Total base number of 60-99
Used oils on which were employed the forward titration	Total base numbers of 3.8-11.0
Used oils which required the back titration	Total base number of 2.9-4.4